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(51) Preparation of metal containing resin composition and antifouling paint containing said resin composition.

(52) A resin composition to be used as a resinous vehicle for an antifouling paint, which is prepared by a method comprising reacting a mixture of

A) said group containing base resin,

B) metallic salt of low boiling organic basic acid, in which the metallic salt is selected from the members having 2 or more valence and lesser oxidation tendency than those of alkali metals, and

C) high boiling organic monobasic acid

at an elevated temperature while removing the formed low boiling organic basic acid out of the system.

Preparation of metal containing resin composition and antifouling paint containing said composition

Field of invention

The present invention relates to a preparation of metal containing resin composition which is characterized by having metal ester bonding at the end portion of pendant chain. The invention also concerns an antifouling paint containing as resinous vehicle the thus formed metal containing resin composition.

Background of the invention

Today, it is very common to apply onto ship's bottom and the like an antifouling coating composition comprising an organic or inorganic antifouling agent and a resinous binder as vinyl resin, alkyd resin and the like.

In that case, since the antifouling effect is fully dependent on the antifouling agent dissolved out of the coating and the dissolution of said agent is primarily a diffusion phenomenon caused by a concentration gradient of said agent in the coating, it is unable to expect a long lasting, stable antifouling effect with them.

Furthermore, since the water insoluble resinous component will, after dissolution of said agent from the coating, form a skeleton structure, there are additional problems as increase in resistance of friction between the ship surface and water, lowering of sailing speed, increase in sailing fuel and the like. Under the circumstances, an antifouling coating composition comprising an antifouling agent and a hydrolyzable resin vehicle capable of forming a comparatively tough coating and being gradually decomposed by hydrolysis in sea water has become the center of public attention.

The present inventors had already found that a class of polyester resins having a number of metal-ester bondings in their polyester backbone chains are useful as a resinous vehicle in a polishing type antifouling paint, and applied for patent as Japanese Patent Application Nos. 165922/81 and 196900/83.

Such resins are of the nature of being easily hydrolyzed, under weak alkaline condition as in sea water, at the metal-ester bonding portions, disintegrated to a number of small, low molecular weight segments and dissolved in sea water. However, said resins are primarily of comparatively low molecular weight (e.g. up-to about 3000) and are poor in film-forming property, and therefore, said coating compositions still have the problems of easy occurrence of cracks and peeling of the formed coatings.

If the molecular weight of said polyester resin is increased to a moderate level, it is indeed possible to improve the film-forming property, but, at that time, it will necessarily be attended with a marked decrease in hydrolysis property of the resin. To compensate the same, if the metal-ester bonding in the backbone chain of the resin is increased in number, there will give additional problems that the resulted resin is only soluble in a polar solvent and not in most solvents commonly used in a coating composition, and that the formed coating is swollen with sea water. These attempts would therefore, give no fruitful results, and thus, there leaves much to be desired.

An attempt has also been made to use a resin whose side chain has a trialkyl tin ester portion as a terminal group. In this type of resin, polarity of the resin is gradually increased in proportion to the progress in hydrolysis of said ester portion, and the resin is finally dissolved in sea water.

Typical examples of such resins are acrylic resins having as a constitutional element tri organo tin salts of α , β -unsaturated basic acids. In this case, in order to obtain a stabilized, tough coating, the resin should preferably be free from hydrophilic groups if circumstances allow, and in order to ensure the dissolution of the hydrolyzed resin in sea water, the resin should preferably have as many hydrophilic groups as possible, i.e. more than a certain critical range, after said hydrolysis.

Therefore, in the preparation of such resin by the copolymerization of tri organo tin salt of α , β -unsaturated basic acid and other acrylic vinyl monomers, attempts have been made such that the former is presented in a higher concentration in the reaction system and the latter is selected from the members with no or least amount of hydrophilic groups. Thus, a copolymer of acrylate, acrylamide, styrene and the like containing 55 to 70 wt% of tri organo tin salt of α , β -unsaturated monobasic acid has been prepared and practically used.

In this type of resin, differing from the aforesaid polyester resin having metal-ester bondings in its main chain, hydrophilic carboxyl groups are generated at the time when the tri organo tin portions at the side chains are released through hydrolysis and the resin is only dissolved in sea water at the stage where the

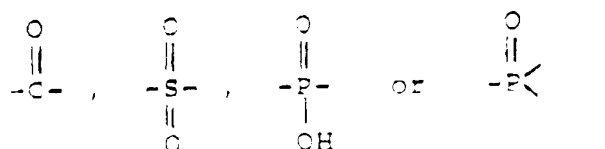
concentration of said carboxy groups get to a certain critical point. The film-forming property of the resin is also excellent, however, there includes a problem that a considerable quantity of highly expensive and toxic organic compound is also essential. Therefore, from both hygienic and economic point of view, it has been urged for cutting the amount of utilizing the use of such material.

Under the circumstances, the inventors have offered previously Japanese Patent Application No. 109434-85, as a hydrolyzable resin composition which has an excellent film-forming property, and whose resin is characterized by having at the side chain portion a particular group capable of resulting a hydrophilic group through hydrolysis, being hydrolyzed and dissolved in sea water at an appropriate rate, and being prepared without the necessity of using a tri-organic tin compound which is expensive and toxic material, a composition consisting essentially of a resin having at least one side chain bearing at least one

terminal group of the formula:

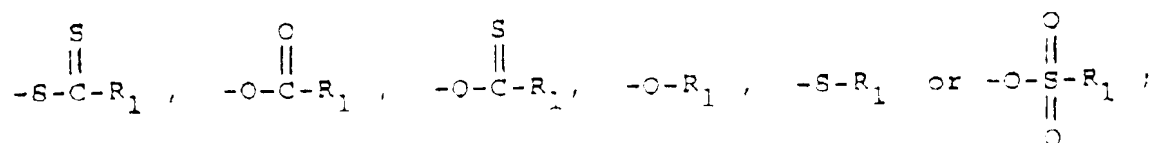


wherein X represents



M is a metal selected from zinc, copper and tellurium;

x is an integer of 1 to 2; R represents an organic acid residue selected from



and R₁ is a monovalent organic residue.

The said resin composition has been prepared by either one of the following methods.

(1) A mixture of (a) a metal oxide, hydroxide, sulfide or chloride, (b) a monovalent organic acid or its alkali metal salt, and (c) a polymerizable unsaturated organic acid or its alkali metal salt is heated under stirring at a temperature lower than the decomposition temperature of the desired metal ester and product, and the by-product substances (as alkali metal chloride, water, monovalent organic acid metal ester, if functional polymerizable unsaturated organic acid salt and the like) are removed to obtain a purified metal ester between the polymerizable unsaturated organic acid and the monovalent organic acid.

Thus obtained metal ester between the polymerizable unsaturated organic acid and the monovalent organic acid or the mixture of said metal ester and the monovalent organic metal ester is then subjected to a homopolymerization or a copolymerization with other polymerizable monomer(s) to give the desired resin having at least one side chain bearing at least one metal ester containing terminal group.

(2) A mixture of (a) a resin having a side chain in organic acid or its alkali metal salt, (b) a metal oxide, hydroxide, sulfide or chloride, and (c) a monovalent organic acid is heated under stirring at a temperature lower than the decomposition temperature of the desired metal ester containing resin, and the over-heated substances are removed if desired to obtain a resin having at least one side chain bearing the desired metal ester terminal group.

(3) Alternatively, the desired product may be prepared by reacting a resin having at a side chain an organic acid or its alkali metal salt and a monovalent organic acid metal ester at a temperature higher than the decomposition temperature of the desired product compound, if using an ester exchange reaction between the metal esters.

It would be thus understood that the present invention is a novel material. The present invention is characterized in that, as a resin, the desired metal ester compound is obtained by a homopolymerization or a copolymerization of at least one polymerizable monomer with a monovalent organic acid metal ester.

Furthermore, the present invention is characterized in that, as a monovalent organic acid metal ester, the desired product compound is obtained by a homopolymerization or a copolymerization of at least one polymerizable monomer with a monovalent organic acid metal ester.

In the second method, since the reaction involved is a neutralization reaction, there is a considerable difficulty in the control of reaction speed and in the extreme case, there occurs gelation of the reaction product.

And, in this third method, since the reaction involved is a kind of equilibrium reaction and no particular regard is paid to removed by-produced monobasic acid out of the reaction system, such acid always remain in the product in the form of free acid and causes blisters in the coating exposed to ionic atmosphere. Furthermore, such acid may be reacted with an antifouling agent in a coating composition under preparation and storage conditions, causing a remarkable decrease in quality of the coating composition or the coating prepared therefrom. Free acid may also cause corrosion of base plate.

It is, therefore, an object of the invention to provide a novel method for the preparation of a metal containing resin composition which is totally free from the abovesaid problems. An additional object of the invention is to provide a method in which a variety of metals may be freely used and such metal can be incorporated in a resin in various forms bonded with carboxylic acid, sulfonic acid and phosphoric acid.

A further object of the invention is to provide a method by which a high boiling organic basic acid can be introduced in side chains of a resin in metal ester form and in a higher reaction yield.

Yet another object of the invention is to provide an antifouling paint which is excellent in film-forming property, and capable of resulting a coating with no blister and being excellent in polishing and antifouling effects.

Summary of the invention

According to the invention, the aforesaid objects can be attained with a process for preparing metal containing resin composition comprising reacting a mixture of (A) acid group containing base resin, (B) metallic salt of low boiling organic basic acid in which the metal is selected from the members having 2 or more valence and lesser ionization tendency than those of alkali metals, and (C) high boiling organic monobasic acid at an elevated temperature while removing the formed low boiling organic basic acid out of the system, and an antifouling paint containing as resinous vehicle and aforesaid resin composition.

Preferred embodiments of the invention

In the present invention, a base resin having acid groups as carboxylic acid, sulfonic acid or phosphoric acid residue is reacted with a metallic salt of low boiling organic basic acid and a high boiling organic monobasic acid at an elevated temperature and the by-produced (through ester exchange reaction) low boiling organic basic acid is removed out of the system through, for example, thermal decomposition, vacuum distillation, azeotropic distillation with water or organic solvent and the like.

The reactions involved are all equilibrium reactions and they are, differing from a vigorous neutralization reaction, easily controlled. Furthermore, there is no fear of remaining a quantity of undesired low boiling basic acid in the reaction product and there is no problem of requiring a larger quantity of initiator.

Therefore, the present method is very useful for the preparation of hydrolysis type, metal containing resin composition for coating use.

Additional benefit resides in the point that high boiling organic acid can be easily and advantageously introduced in a base resin through metal ester bonding, which is hardly possible by the conventional ester exchange reaction between an acid group containing base resin and metallic ester of organic monobasic acid.

The base resin used in the present invention may be any of the known, coating-use resin having acid groups at the side chains thereof. Examples are vinyl resin, polyester resin, alkyd resin, epoxy resin and the like.

The metallic salts of low boiling basic acids are metallic salts of organic carboxylic acids, organic sulfonic acids or organic phosphoric acids each having a boiling point of 100° to 240° C. Said metallic component may be any metals having 2 or more valence and lesser ionization tendency than those of alkali metals.

Examples are the members belonging to Ib (e.g. Cu, Ag), IIa (e.g. Ca, Ba), IIb (e.g. Zn, Cd, Hg), IIIa (e.g. Sc, Y), IIIb (e.g. Al, In), IVa (e.g. Ti, Zr), IVb (e.g. Sn, Pb, Si), Va (e.g. V, Nb), VIa (e.g. Cr, Mo, W), VIb (e.g. Se, Te), VIIa (e.g. Mn) and VIII (e.g. Fe, Co, Ni) groups of Periodic Table.

Though the metallic salts may likewise be organic metal salts such as diethyl tin acetate, diisobutyl tin acetate and the like, they must be of polyorganic salt type.

In this invention, the term "low boiling" is used in contrast to the term "high boiling", and there is no definite limitation of the boiling range of the respective organic basic acid. However, in practice, the low boiling organic basic acid should preferably have a boiling point of 100°C to 240°C.

In general, a metallic salt is liable to be decomposed by heating. Therefore, the reaction temperature must be settled in a range which is lower than the decomposition temperature of the metallic salt used.

For this reason, the low boiling organic basic acid should preferably be easily removed out of the system at a temperature which is lower than the decomposition temperature of the metallic salt and preferably 130°C or more, by either method of thermal decomposition, vacuum distillation, azeotropic distillation with water or azeotropic distillation with an organic solvent.

Particularly preferable low boiling organic acids are acetic acid, propionic acid, oxalic acid, lactic acid, pyruvic acid, valeric acid, dimethyl acetic acid, ananthic acid, bicyclopentane carboxylic acid, citric acid, glycolic acid, acrylic acid, methacrylic acid and the like. Their corresponding sulfuric acids and phosphoric acids may likewise be used advantageously.

The metallic salts of low boiling organic basic acids may easily be prepared by the equimolar reaction of metal hydroxide or oxide and an organic basic acid, or the equimolar reaction of metallic sulfonate, nitrate or halide and an alkali metal salt of organic basic acid.

Various metallic salts of low boiling organic basic acids are available in the market, too.

As the high boiling organic monobasic acid, it should preferably have a far higher boiling point, at least 20°C higher boiling point, than that of the low boiling organic acid. More preferably, it should have a bioactivity as fungicidal, antifouling and other similar activities. They may be any organic acids including aliphatic, aromatic, alicyclic and heterocyclic organic acids.

Typical examples are benzoic acid, salicylic acid, 3,5-dichlorobenzoic acid, lauric acid, stearic acid, nitrobenzoic acid, indoleic acid, naphthoic acid, 12-hydroxy stearic acid, fluorobenzoic acid, sulvic acid, adipic acid, mercaptobenzoic acid, O-cresotinic acid, naphthol-1-carboxylic acid, p-phenyl benzene sulfonic acid, p-oxy-benzoic acid, chloroacetic acid, monochloroacetic acid, naphthenic acid, 3-naphthalene sulfonic acid, naphthol-1-sulfonic acid, 5-chloro-4, 4-bis (3,5-dichloro-2-hydroxy phenyl) toluene sulfonic acid, p-phenyl benzoic acid, p-toluene sulfonic acid, p-benzene chlorosulfonic acid, dimethyl dithio carbamic acid, diethyl dithio carbamic acid, dibutyl dithio carbamic acid, lithocholic acid, chloroxy acetic acid, 2,4-dichlorophenoxy acetic acid, oleic acid, versatic acid, nicotinic acid, penicillic acid and the like. The reaction may be easily proceeded by merely mixing the materials and heating the mixture. At that time, it is however, necessary to continuously remove the formed low boiling organic basic acid out of the system (i.e., for example, thermal decomposition, vacuum distillation, azeotropic distillation with water or an organic solvent and the like).

The inventors have also found that the reaction time could be markedly shortened when the reaction is carried out in the presence of 0.01 to 5% by weight, preferably 0.03 to 2% by weight of the resinous acid or an organic tin catalyst or an acid catalyst.

Thus, obtained resin composition is stable and free from a detectable amount of low boiling organic basic acid which will cause blisters in the formed film or coating. Since an amount of metal ester bondings are included, thus formed film or coating can be hydrolyzed under acidic atmosphere.

Therefore, the present resin composition may be used in various form coatings, including paint, modifone and agricultural chemical industries, as hydrolyzable, film-forming resin. Among them, particular preference is given to resinous varnish or an antifouling paint.

Thus, in the second aspect of the invention, is provided an antifouling paint containing as resinous varnish a metal containing resin prepared by the method of this invention.

In this particular application, since a hydrolysis rate of the resulting coating is very important, the acid group containing base resin should preferably have an acid value of 25 to 350 mg KOH/g. This is because, if the acid value is less than 25 g KOH/g, the wished hydrolysis rate of the coating may not be fully attained due to deficient metal ester bondings, whereas, if the acid value exceeds over 350 mg KOH/g, there are adverse effects on film properties.

As to the molecular weight of the present metal containing resin, there is no particular limit, but, however, when used as a resinous varnish or an antifouling paint, the average molecular weight of the resin should preferably be settled in a range of 4000 to 40000 and more preferably 10000 to 30000. If the molecular weight of the resin is less than 1000, there is a risk of the occurrence of cracks and peeling of the formed coating, and, if the molecular weight is more than 40000, the average molecular weight of the resin exceeds over 40000, there is a risk of the occurrence of cracks and peeling of the formed coating. Therefore, the molecular weight of the resin should be settled in a range of 4000 to 40000 and more preferably 10000 to 30000. The molecular weight of the resin can be determined by the method of gel permeation chromatography (GPC) or the method of end group analysis (EGA).

The present antifouling paint is characterized by containing as resinous vehicle the abovementioned metal containing resin composition, and however, this paint may further contain, as option ingredients, the following.

(1) Antifouling agent:

Various known antifouling agents including antifouling agents for ship bottom paint, bactericides, fungicides, agricultural chemicals or the like may be satisfactorily used. However, when the solubility of such compound in sea water is less than 0.01 ppm, it is unable to get a good balance between the dissolution speed of the coating and dissolving power of the antifouling agent, and therefore, no effective antifouling can be expected with said compound. On the other hand, when the solubility of such compound in sea water is over 5000 ppm, the formed coating will absorb water and the contained antifouling agent will selectively dissolve out and hence, it is unable to get a desired antifouling efficiency.

Therefore, the solubility of antifouling agent in sea water should preferably be in a range of 0.01 to 5000 ppm, and more preferably 0.1 to 50 ppm.

Examples of such antifouling agents are powder or flake form of copper, zinc, manganese or the like; oxides, suboxides, rhodanides, carbamates, hydroxides or pyrithiones of copper, zinc, manganese and the like; benzothiazole compounds; phthalimide compounds; sulfamide compounds; sulfide compounds; quinoline compounds; phthalonitrile compounds; carbamate compounds; isothiazoline compounds; triphenyl tin compounds; carbamic acid compounds and esters; thiocyanate compounds and the like.

More specifically, they must be classified in the following groups from the sustained-release point of view.

(A) most preferable members:

copper powder, copper suboxide, copper rhodanide, zinc bis (dimethyl dithiocarbamate), zinc ethylene bis (dithiocarbamate), manganese ethylene bis (dithiocarbamate), copper bis (dimethyl dithiocarbamate), 2-thiocyanomethylthio benzothiazole, tetramethyl thiuram disulfide, 8-hydroxy quinoline, zinc pyrithione, N-(fluorodichlorothio) phthalimide, 2,4,5,6-tetrachloro-1,3-isophthalonitrile, 2,3,5,6-tetrachloro-4-(methylsulfonyl) pyridine, N,N-dimethyl-N'-phenyl-N'-(fluorodichlorothio) sulfamide, 3-jodo-2-propynyl butyl carbamate, 4,5-dichloro-2-n-octyl-4-isothiazoline-3-on and the like,

(B) preferable members:

copper hydroxide, triphenyl tin hydroxide, triphenyl tin chloride, zinc powder, N-(trichloromethylthio)-phthalimide, N-(tetrachloroethylthio)-tetraphthalimide, N,N-dimethyl-N'-(fluorodichloromethylthio)-sulfamide, 2-benzimidazole carbamic acid methyl, benzyl isothiocyanate, N-n-octyl-isothiazolone, dimethyl dithiocarbamic bromide and the like.

(C) least preferable members:

bistriphenyl tin oxide, quinoline, triphenyl tin acetate, zinc hydroxide and the like.

At least one of the abovesaid antifouling agents may be advantageously used. Other antifouling agents may be used together, as desired.

Among them copper powder is very useful when combined with other antifouling agent, because of exhibiting a synergistic effect and providing a good storage stability. When an antifouling agent is compounded with heretofore proposed triorgano tin salt of high molecular weight substance (known hydrolysis type resin), there are often reactions between the resin and the antifouling agent used. However, the present resinous vehicle is inert to these antifouling agents, and therefore, it is possible to get a stable coating composition and a reliable antifouling efficiency of the coating.

(2) Plasticizer and hydrolysis regulator:

As the plasticizer and hydrolysis regulator, any of the known members having solubility in sea water of 1 to 10% by weight may be satisfactorily used.

This is because, if the solubility is over 10% by weight, the used plasticizer and hydrolysis regulator are selectively dissolved out of the coating in sea water and such a plasticizing and softening effects can hardly be obtained. Examples of such plasticizers are phthalic acid esters as diethyl phthalate, dimethyl phthalate, dicyclohexyl phthalate and the like; aliphatic dibasic acid esters as diisobutyl adipate, diethyl sebacate and the like; glycol esters as diethylene glycol dibenzoate, pentaerythritol alkyl ester and the like; phosphoric acid esters as triethyl phosphite, bis-diethyl phosphite and the like; epoxy fatty acid esters as epoxy soyabean oil, epoxy octyl stearate and the like; organotin plasticizers as dioctyl tin sebacate, dibutyl tin aurate and the like; triethyl trimellitate, camphor, triacetylene and the like.

3) Hydrolysis regulator:

Examples of such hydrolysis regulators are chlorinated paraffin, polyvinyl ether, polyacryloyl sebacate, partially hydrogenated terphenyl, polyvinyl acetate, polyalkyl methacrylate, polyether polyalkyl resin, polyester resin, polyvinyl chloride and the like.

(4) Pigment:

For example, body pigments as baryte, precipitated calcium sulphate, talc, kaoline, chalk, silica white, alumina white, titanium white, bentonite and the like; color pigments as titanium peroxide, chromium oxide, basic lead sulfate, tin oxide, carbon black, graphite, red iron oxide, chrome green, emerald green, phthalocyanine blue, and the like.

(5) Solvent:

For example, hydrocarbons (e.g., xylene, toluene, benzene, ethyl benzene, cyclopentane, octane, heptane, cyclohexane, white spirit and the like), ethers (e.g., dioxan, tetrahydrofuran, ethylene glycol monomethyl ether, ethylene glycol dimethyl ether, dimethoxy ethane, ethylene glycol monomethyl ether, ethylene glycol dibutyl ether, diethyl ether, diisobutyl ether, diethylene glycol monomethyl ether and the like), esters (e.g., butyl acetate, propyl acetate, benzyl acetate, ethylene glycol dimethyl ether acetate, ethylene glycol monomethyl ether acetate and the like), ketones (e.g., methyl isobutyl ketone, ethyl isobutyl ketone and the like), alcohols (e.g., n-butanol, propyl alcohol and the like), and the like.

(6) Other additives:

For example, organic monobasic acids (e.g., formic, malic, citric, tartaric, succinic and the like), ammonium phosphate, and the like.

The present antifouling paint can be prepared by the method known per se in the art, by using said film-forming and non-film-forming materials and the like.

The present inventors have also found that by the use of about 0.1 to 6 wt% of amphoteric group-containing compound as described in Japanese Patent Application (aid. No. 181727-58) in the present coating composition, as exemplified in Examples 19 to 59, it is possible to shorten the drying time required for the formulation of said paint and improve the dispersion stability of thus obtained paint. Since the vehicle resin contains metals, whose oxidation tendency is lower than those of alkali metals (e.g., sodium, lithium and the like) in the form of metal esters, the coating is not obtained well probably by the use of such alkali compounds as in the above-mentioned prior art, and the use of amphoteric compound is effective.

Furthermore, differing from the known compound described in the prior art, the compound used in the present invention is characterized by having the most active amphoteric group in the molecule.

Therefore, with the progress of the time, it will be possible to make the vehicle resin and the amphoteric compound more effective, and it is expected that the use of the compound will be wider and wider. To be the most effective, the compound should have a high molecular weight, and it is expected that the use of the compound will be wider and wider. To be the most effective, the compound should have a high molecular weight, and it is expected that the use of the compound will be wider and wider.

Furthermore, since the present antifouling paint can be formulated without the necessity of being fully relied on an expensive and toxic triorgano tin compound, the manufacturing cost can be markedly lowered and hygienic problems can be effectively obviated.

The present paint is totally free from low boiling organic basic acid and therefore, there is no fear of forming blisters in the formed coating. Thus, the present antifouling paint is quite useful for the coating of various substrates as ships, marine structures, fish nets and the like.

The invention shall be now more fully explained in the following Examples. Unless otherwise being stated, all parts and % are by weight.

Preparation of base resin varnishes

Reference Example 1

Into a 4-necked flask fitted with a stirrer, a reflux condenser, a nitrogen gas inlet tube and a dropping funnel, were placed 100 parts of xylene and 20 parts of n-butanol and the mixture was heated to 110° to 110° C. To this, a mixture of 25.7 parts of acrylic acid, 57.8 parts of ethyl acrylate, 16.5 parts of methyl methacrylate and 3 parts of azobisisobutyronitrile was dropwise added in 4 hours. After completion of said addition, the combined mixture was maintained at 110° C for 30 minutes, added dropwise with a mixture of 20 parts of xylene, 10 parts of n-butanol and 0.5 part of azobisisobutyronitrile in 1 hour and then maintained at the same temperature for 2 hours to obtain a resinous varnish (A) having a solid content of 39.6 wt % and a solid acid value of 200 mg KOH/g. The number average molecular weight (polystyrene conversion) of the resin contained was 11000.

Reference Example 2

Into a 4-necked flask fitted with a reflux condenser, a stirrer, a nitrogen gas inlet tube and a dropping funnel, were placed 90 parts of xylene and 20 parts of n-butanol and the mixture was heated to 100° to 110° C. To this, a mixture of 7.7 parts of methacrylic acid, 64.4 parts of methyl methacrylate, 28 parts of 2-ethyl hexyl acrylate and 2 parts of azobisisobutyronitrile was dropwise added in 4 hours. After completion of said addition, the mixture was heated at 110° C for 30 minutes, added dropwise with a mixture of 30 parts of xylene, 10 parts of n-butanol and 0.5 part of azobisisobutyronitrile in 1 hour and then heated at the same temperature for 2 hours to obtain a resinous varnish (B) having a solid content of 39.8 wt % and a solid acid value of 50 mg KOH/g. The number average molecular weight of the resin contained was 15000.

Reference Example 3

Into a 4-necked flask fitted with a reflux condenser, a stirrer, a nitrogen gas inlet tube and a dropping funnel, were placed 100 parts of xylene and 20 parts of n-butanol and the mixture was heated to 100° to 110° C. To this, a mixture of 38.5 parts of acrylic acid, 50.9 parts of ethyl acrylate, 10.6 parts of n-butyl acrylate and 3 parts of azobisisobutyronitrile was dropwise added in 4 hours. After completion of said addition, the mixture was heated at 110° C for 30 minutes, dropwise added with a mixture of 20 parts of xylene, 10 parts of n-butanol and 0.5 part of azobisisobutyronitrile in 1 hour and then heated at the same temperature for 2 hours to obtain a resinous varnish (C) having a solid content of 39.4 wt % and a solid acid value of 300 mg KOH/g. The number average molecular weight of the resin contained was 12000.

Reference Example 4

Into a 4-necked flask fitted with a reflux condenser, a stirrer, a nitrogen gas inlet tube and a dropping funnel, were placed 80 parts of xylene and 20 parts of n-butanol and the mixture was heated to 80° to 90° C. To this, a mixture of 38.5 parts of acrylic acid, 45.8 parts of ethyl acrylate, 15.7 parts of methyl methacrylate and 1.5 parts of azobisisobutyronitrile was dropwise added in 4 hours. After completion of said addition, the mixture was heated at 90° C for 30 minutes, dropwise added with a mixture of 40 parts of xylene, 10 parts of n-butanol and 0.5 parts of azobisisobutyronitrile in 1 hour and then heated at the same

temperature for 2 hours to obtain a resinous varnish (D) having a solid content of 63.8 wt% and a solid acid value of 600 mg KOH/g. The number of average molecular weight of the resin obtained was 37000.

4 Example 1

Into a 4-necked flask fitted with a reflux condenser, a stirrer, a nitrogen gas inlet tube and a decanter were placed 100 parts of the resinous varnish (A) obtained in Reference Example 1, 25.9 parts of zinc acetate, 40.3 parts of acetic acid and 120 parts of xylene and the mixture was heated to 120°C and maintained at the same temperature while removing the formed acetic acid with said solvent. The end point of said reaction was settled by determining the quantities of acetic acid in the distillate and the reaction was stopped after elapsing 12 hours. Thus obtained varnish-1 had a solid content of 55.3 wt% and a viscosity of R-5.

15 Example 2

Into a 4-necked flask fitted with a reflux condenser, a stirrer, a nitrogen gas inlet tube and a decanter were placed 100 parts of the resinous varnish (C) obtained in Reference Example 3, 44 parts of cadmate propionate, 60 parts of naphthoic acid, 0.1 part of butane sulfonyl acid and 20 parts of deionized water and the mixture was heated to 100°C and maintained at the same temperature while removing the formed propionic acid azeotropically with water. The end point of said reaction was determined by checking the amount of propionic acid in the distillate. The remaining amounts of water were completely removed, the reaction was stopped after 7 hours' reaction and xylene was then added to the reaction mixture. Thus obtained varnish-2 had a solid content of 52.3 wt% and a viscosity of P.

Example 3

Into a 3-necked flask fitted with a reflux condenser, a stirrer and a decanter, were placed the resinous varnish (B) obtained in Reference Example 2, 3.1 parts of manganese acetate and 7.3 parts of 2,4-dichlorophenoxy acetate and the mixture was heated to 70°C and maintained at the same temperature for 10 hours. The formed acetic acid was continuously removed under reduced pressure and, after completion of the reaction, 95 parts of xylene were added to obtain varnish-3 having a solid content of 50.3 wt% and a viscosity of U.

Example 4

Into a similar reaction vessel as used in Example 1, were placed 100 parts of the resinous varnish (D) obtained in Reference Example 4, 37.2 parts of cobalt acetate, 12.4 parts of versatic acid and 120 parts of xylene and the mixture was heated and reacted while removing the formed acetic acid with the solvent for 12 hours. Thus obtained varnish-4 had a solid content of 56.2 wt% and a viscosity of R.

25 Example 5

The similar experiment as stated in Example 4 was repeated excepting substituting 95.1 parts of germanium acetate for 37.2 parts of cobalt acetate and 196 parts of versatic acid for 12.4 parts of versatic acid. Thus obtained varnish-5 had a solid content of 54.4 wt% and a viscosity of L.

Example 6

Into a 4-necked flask fitted with a reflux condenser, a stirrer, a nitrogen gas inlet tube and a decanter were placed 100 parts of the resinous varnish (A) obtained in Reference Example 1, 20 parts of cobalt acetate, 100 parts of germanium acetate, 100 parts of versatic acid and 120 parts of xylene and the mixture was heated and reacted while removing the formed acetic acid with the solvent for 12 hours. Thus obtained varnish-6 had a solid content of 54.4 wt% and a viscosity of L.

varnish-6 had a solid content of 52.8 wt% and a viscosity of P.

Example 7

Into a 4-necked flask fitted with a reflux condenser, a stirrer, a nitrogen gas inlet tube and a decanter, were placed 100 parts of the resinous varnish (A) obtained in Reference Example 1, 42.5 parts of zinc di-lactate trihydrate, 28.6 parts of SA-13 (trademark of Idemitsu Sekiyu, branched type monocarboxylic acid, average carbon number 13) and 100 parts of xylene and the mixture was heated to 120°C and reacted at the same temperature while removing the formed lactic acid with xylene. Thus obtained varnish-7 had a solid content of 54.2 wt% and a viscosity of Q.

Example 8

Into a 4-necked flask fitted with a reflux condenser, a stirrer, a nitrogen gas inlet tube and a decanter, were placed 100 parts of the resinous varnish (A) obtained in Reference Example 1, 37 parts of nickel valerate, 22.6 parts of SA-9 (trademark of Idemitsu Sekiyu, branched type monocarboxylic acid, average carbon atoms 9), and 95 parts of xylene and the mixture was heated to 140°C and reacted at the same temperature while removing the formed valeric acid with xylene. Thus obtained varnish-8 had a solid content of 55.1 wt% and a viscosity of O.

Example 9

The same procedures as stated in Example 3 were repeated excepting substituting a mixture of 100 parts of the resinous varnish (C) obtained in Reference Example 3, 99.1 parts of lead enanthate and 62 parts of versatic acid for the materials shown in Example 3 and changing the reaction temperature to 140°C. Thus obtained varnish-9 had a solid content of 52.7 wt% and a viscosity of R.

Example 10

Into a 4-necked flask fitted with a reflux condenser, a stirrer, a nitrogen gas inlet tube and a decanter, were placed 100 parts of the resinous varnish (B) obtained in Reference Example 2, 9.9 parts of magnesium cyclohexane carboxylate, 4.4 parts of nicotinic acid and 20 parts of deionized water and the mixture was reacted as in Example 2. Thus obtained varnish-10 had a solid content of 53.4 wt% and a viscosity of R.

Example 11

Into a 4-necked flask fitted with a reflux condenser, a stirrer, a nitrogen gas inlet tube and a decanter, were placed 100 parts of the resinous varnish (A) obtained in Reference Example 1, 39.9 parts of aluminium cyclopropane carboxylate, 72.4 parts of 2,4-dichlorophenoxy acetate and 125 parts of xylene and the mixture was heated to 140°C and reacted as in Example 1, to obtain varnish-11 having a solid content of 51.8 wt% and a viscosity of V.

Example 12

Into a 4-necked flask fitted with a reflux condenser, a stirrer, a nitrogen gas inlet tube and a decanter, were placed 100 parts of the resinous varnish (A) obtained in Reference Example 1, 34.7 parts of tellurium acetate, 40 parts of naphthenic acid, 0.2 part of butylene sulfonic acid and 110 parts of xylene and the mixture was reacted as in example 1 for 8 hours to obtain varnish-12 having a solid content of 52.4 wt% and a viscosity of S.

Example 13

into a 4-necked flask fitted with a reflux condenser, a stirrer, a nitrogen gas inlet tube and a decanter, were placed 100 parts of the resinous varnish (B) obtained in Reference Example 2, 10.4 parts of dibutyl tin acetate, 7.1 parts of SA-13 and 115 parts of xylene and the mixture was reacted as in Example 1 to obtain varnish-13 having a solid content of 53.4 wt% and a viscosity of V.

Example 14

into a 4-necked flask fitted with a reflux condenser, a stirrer, a nitrogen gas inlet tube and a decanter, were placed 100 parts of the resinous varnish (A) obtained in Reference Example 1, 32.4 parts of chromium acetate, 83.7 parts of maleic acid and 130 parts of xylene and the mixture was reacted as in Example 1 to obtain varnish-14 having a solid content of 51.8 wt% and a viscosity of U.

Example 15

into a 4-necked flask fitted with a reflux condenser, a stirrer, a nitrogen gas inlet tube and a decanter, were placed 100 parts of the resinous varnish (D) obtained in Reference Example 4, 62.1 parts of dibutyl tin acetate, 62.1 parts of versatic acid and 150 parts of xylene and the mixture was reacted as in Example 1 to obtain varnish-15 having a solid content of 54.7 wt% and a viscosity of X.

Example 16

Using a resinous varnish (B) obtained in Reference Example 2, 10 parts of titanium acetate, 18.2 parts of peribellonic acid and 50 parts of xylene and the reaction temperature of 75° to 90° C, the similar experiment as stated in Example 3 was repeated to obtain varnish-16 having a solid content of 52.6 wt% and a viscosity of Y.

Example 17

into a 4-necked flask fitted with a reflux condenser, a stirrer, a nitrogen gas inlet tube and a decanter, were placed 100 parts of the resinous varnish (C) obtained in Reference Example 3, 59.9 parts of titanium acetate, 101 parts of 2,4-dichlorophenylacetic acid and 180 parts of xylene and the mixture was reacted as in Example 1 to obtain varnish-17 having a solid content of 56.2 wt% and a viscosity of Z.

Example 18

into a 4-necked flask fitted with a reflux condenser, a stirrer, a nitrogen gas inlet tube and a decanter, were placed 100 parts of the resinous varnish (D) obtained in Reference Example 4, 40 parts of dibutyl tin acetate, 60 parts of nadicmethacrylic acid and 140 parts of xylene and the mixture was heated at 120° C while stirring the formed acid add with the solvent. Thus obtained varnish-18 had a solid content of 53.6 wt% and a viscosity of W.

Comparative Example 1

The resinous varnish (C) obtained in Reference Example 3 was used as the comparative varnish (C).

Comparative Example 2

Using a 4-necked flask fitted with a reflux condenser, a stirrer, a nitrogen gas inlet tube and a decanter, were placed 100 parts of the resinous varnish (C) obtained in Reference Example 3, 10 parts of titanium acetate, 18.2 parts of peribellonic acid and 50 parts of xylene and the mixture was reacted at 75° to 90° C, the similar experiment as stated in Example 3 was repeated to obtain comparative varnish-1 having a solid content of 52.6 wt% and a viscosity of Y.

110°C for 30 minutes, a mixture of 20 parts of xylene, 10 parts of n-butanol and 0.5 part of azobisisobutyronitrile was dropwise added in 1 hour and the combined mixture was heated at the same temperature for 2 hours to obtain Comparative varnish 3 having a solid content of 39.6 wt%.

Comparative Example 3

Into a 4-necked flask fitted with a reflux condenser, a stirrer, a nitrogen gas inlet tube and a decanter, were placed 100 parts of the resinous varnish (A) obtained in Reference Example 1, 10.3 parts of zinc hydroxide, 60 parts of oleic acid and 110 parts of xylene and the mixture was heated at 100 to 120°C while removing water with the solvent. Thus obtained varnish (Comparative varnish-3) had a solid content of 55.8% and a viscosity of Z₂.

Comparative Example 4

Into a 3-necked flask fitted with a reflux condenser, a stirrer and a nitrogen gas inlet tube, were placed 100 parts of the resinous varnish (A) obtained in Reference Example 1 and 68 parts of zinc oleate, and the mixture was reacted at 120°C for 3 hours. Thus obtained varnish (Comparative varnish-4) had a solid content of 62% and a viscosity of M to N.

Comparative Example 5

Into a 4-necked flask fitted with a reflux condenser, a stirrer, a nitrogen gas inlet tube and a decanter, were placed 100 parts of the resinous varnish (A) obtained in Reference Example 1, 13 parts of zinc hydroxide and 105 parts of xylene and the mixture was heated at 120°C. During the reaction, certain amounts of water were distilled off, but after elapsing 30 minutes from the commencement of said reaction, the content was turned to gel and no uniform resinous solution was obtained.

Comparative Example 6

Into a similar reaction vessel as used in Comparative Example 1, were placed 100 parts of the resinous varnish (D) obtained in Reference Example 4, 16.6 parts of copper hydroxide, 60 parts of naphthenic acid and 110 parts of xylene and the mixture was heated at 120°C while removing water with the solvent. After elapsing 2 hours from the commencement of the reaction, the content was turned to gel and no uniform resinous solution was obtained.

Example 19

45 parts of varnish-1 obtained in Example 1, 30 parts of cuprous oxide, 5 parts of zinc bis (dimethyl dithiocarbamate), 3 parts of colloidal silica, 5 parts of xylene, 10 parts of methyl isobutyl ketone and 2 parts of n-butanol were placed in a ball mill and the mixture was subjected to a dispersion operation for 5 hours to obtain a coating composition containing particles with maximum diameter of 35μ.

Example 20 to 58 and Comparative Examples 5 to 9

Using the materials shown in Table 1 and following the method stated in Example 19, the respective coating composition was prepared.

Table 1

	Example	20	21	22	23	24	25	26
	varnish 1	35	30					
5	varnish 2			40	45			
	varnish 3					25		
	varnish 4						40	
	varnish 5							35
10	varnish 6							
	varnish 7							
	varnish 8							
	varnish 9							
	varnish 10							
	Note 1	20			15		15	
15	Note 2		20			15		
	Note 3			25				
	Note 4							
	Note 5						3	
	Note 6		10					15
20	Note 7				5			
	Note 8	10						
	Note 9					10		
	Note 10						5	
	Note 11						10	
25	Note 12					5		5
	Note 13							
	Note 14			5				
	Note 15							10
	Note 16		5			10		
30	Note 17							
	Note 18			5				5
	Note 19		5		5			
	Note 20				5	5		
	Note 21			5				
35	Note 22					5		
	Note 23	5	5	5	2			
	Note 24	10		5	5		5	10
	Note 25	5	5	5	5		5	
	Note 26	3	3	3	3	3	3	3
40	Note 27		10					
	Note 28	10	5		5	20	10	10
	Note 29	2	2	2	2	2	4	2
	Total	100	100	100	100	100	100	100

Table 1 (continued)

	Example	27	28	29	30	31	32
5	varnish 1						
	varnish 2						
	varnish 3						
	varnish 4						
	varnish 5						
10	varnish 6	30					
	varnish 7		35				
	varnish 8			30			
	varnish 9				35		
	varnish 10					40	45
15	Note 1	25		30		20	
	Note 2				30		
	Note 3		20				
	Note 4	5					
	Note 5				5		
	Note 6						10
20	Note 7			10		5	
	Note 8					5	
	Note 9						
	Note 10						
	Note 11						
25	Note 12				10		15
	Note 13		10				
	Note 14	5					
	Note 15						
	Note 16				5		
	Note 17		10	5			
30	Note 18	5					10
	Note 19	5	5				
	Note 20	5		5			
	Note 21		5				
	Note 22				5		
35	Note 23	5	5				
	Note 24			5		5	
	Note 25	5					
	Note 26	3	3	3	3	3	3
	Note 27	5		5	5	10	5
40	Note 28		5	5		10	10
	Note 29	2	2	2	2	2	2
	total	100	100	100	100	100	100

[illegible]

Table 1 (continued)

Example	43	44	45	46	47	48	49	50	51
varnish 1									
varnish 2								10	5
varnish 3									
varnish 9									
varnish 10									
varnish 11									
varnish 12									
varnish 13	35								
varnish 14		40							
varnish 15			40						
varnish 16				45					
varnish 17					40				
varnish 18						45	40	30	35
Note 1'	15		15				25	20	
Note 2'		5			15	20			25
Note 3'		10						5	
Note 4'									
Note 5'									
Note 6'									
Note 7'				15					
Note 8'					10				
Note 9'							5		
Note 10'									
Note 11'	10					10	10		
Note 12'			10						5
Note 13'								10	
Note 14'									10
Note 15'	5		5						
Note 16'					10				
Note 17'		10		15					
Note 18'									
Note 19'		5							
Note 20'	10	10	10	15	10	10	10		10
Note 21'		5						15	
Note 22'	5		5		5	5		5	
Note 23'			5		5	5			5
Note 24'	3	3	3		3	3	3	3	3
Note 25'	15	10	5	10			5		
Note 26'	2	2	2		2	2	2	2	2
total	100	100	100	100	100	100	100	100	100

Table 1 (continued)

	Example	52	53	54	55	56	57	58
		35	35	45	45	35	35	40
5	varnish 1							
	varnish 2							
	varnish 3							
	varnish 4							
	varnish 13							
10	varnish 16							
	varnish 17							
	varnish 18							
	Note 1"	5					10	
	Note 2"		10					
15	Note 3"			5	10			
	Note 4"		5					10
	Note 5"	10		10			5	
	Note 6"		5					
	Note 7"		10	15			15	
	Note 8"	15				15		25
20	Note 9"		5					
	Note 10"	5						
	Note 11"				5			
	Note 12"						10	
	Note 13"				5			
25	Note 14"					10		
	Note 15"			5				
	Note 16"	5						
	Note 17"		5					
	Note 18"					10		10
30	Note 19"					5		
	Note 20"	5						
	Note 21"	5	10	5	5		5	10
	Note 22"	5	5	5	10	5	5	
	Note 23"	3	3	3	3	3	3	3
35	Note 24"		10	5	10	15	10	
	Note 25"	5			10			
	Note 26"	2	2	2	2	2	2	2
	total	100	100	100	100	100	100	100

Table 1 (continued)

5	<u>Comparative Example</u>	<u>7</u>	<u>8</u>	<u>9</u>	<u>10</u>	<u>11</u>
	<u>Comparative varnish 1</u>	45				
10	<u>Comparative varnish 2</u>		45			
	<u>Comparative varnish 3</u>			23		
	<u>Comparative varnish 4</u>				45	
15	<u>varnish 1</u>					35
	<u>cuprous oxide</u>	30	30	15	30	
	<u>Zn bis (dimethyl</u>					
20	<u>dithiocarbamate)</u>	5	5	2	5	
	<u>copper sulfate</u>					25
	<u>dioctyl phthalate</u>					5
25	<u>titanium oxide</u>					3
	<u>talc</u>					5
30	<u>xylene</u>	5	5	46	5	10
	<u>colloidal silica</u>	3	3	2	3	3
	<u>red iron oxide</u>					5
35	<u>methyl isobutyl ketone</u>	10	10	10	10	5
	<u>n-butanol</u>	2	2	2	2	2
40	<u>total</u>	100	100	100	100	100

In Comparative Example 7, paint viscosity was very high, and therefore, a larger quantity of xylene was used.

Note 1: cuprous oxide

Note 2: zinc white

Note 3: copper rhodanide

Note 4: Cu powder

Note 5: Zn powder

Note 6: copper hydroxide

Note 7: 2-thiocyanomethylthio benzothiazole

Note 8: N-(fluorodichloromethylthio) phthalimide

Note 9: N-(trichloromethylthio) phthalimide

Note 10: N-(tetrachloroethylthio) tetraphthalimide

Note 11: benzyl isothiocyanate

Note 12: quinoline

Note 13: 8-hydroquinoline

Note 14: zinc pyrithione

Note 15: triphenyl tin acetate

Note 16: bis-triphenyl tin oxide

Note 17: 3-Jod-2-propynyl butyl carbamate

Note 18: tricresyl phosphate

Note 19: polyvinyl ether

Note 20: chlorinated paraffin wax

Note 21: polyether polyol

Note 22: dioctyl phthalate

Note 23: talc

Note 24: titanium oxide

Note 25: red iron oxide

Note 26: colloidal silica

Note 27: methyl isobutyl ketone

- 5 Note 28: xylene ;
Note 29: n-butanol
Note 1': cuprous oxide
10 Note 2': copper rhodanide
Note 3': zinc white
Note 4': copper hydroxide
15 Note 5': N,N-dimethyl-N'-(fluorodichloromethylthio)
 sulfamide
Note 6': 2-benzimidazole carbamic methyl
20 Note 7': benzyl isothiocyanate
Note 8': N-n-octyl-isothiazolone
Note 9': N N-dimethyl-N'-phenyl-N'-(fluorodicyclomethylthio)
25 sulfamide
Note 10': Zn bis (dimethyl dithiocarbamate)
30 Note 11': Zn ethylene bis (dithiocarbamate)
Note 12': Mn ethylene bis (dithiocarbamate)
Note 13': Cu bis (dimethyl dithiocarbamate)
35 Note 14': 2,4,5,6-tetrachloro-1,3-isophthalonitrile
Note 15': 2,3,5,6-tetrachloro-4-(methyl sulfonyl) pyridine
Note 16': 4,5-dichloro-2-n-octyl-4-isothiazoline-3-on
40 Note 17': dimethyl dithiocarbamic acid bromide
Note 18': triphenyl tin hydroxide
Note 19': triphenyl tin chloride
45 Note 20': chlorinated paraffin wax
Note 21': dioctyl phthalate
50 Note 22': titanium oxide
Note 23': red iron oxide
55

Note 24': colloidal silica

Note 25': xylene

Note 26': n-butanol

Note 1'': chlorinated polyethylene

Note 2'': chlorinated polypropylene

Note 3'': asiamyl citrate

Note 4'': isobutyl tartarate

Note 5'': polyether polyol

Note 6'': copper naphthenate

Note 7'': cuprous oxide

Note 8'': zinc white

Note 9'': 2,4-(thiazolyl) benzimidazole

Note 10'': 5-ethoxy-3-trichloromethyl-1,2,4-thiadiazole

Note 11'': phenothiazole

Note 12'': α -nitrostyrene sulfathiazole

Note 13'': nitro acridine

Note 14'': sulfathiazole

Note 15'': tetraphenyl boron pyridinium

Note 16'': thiabenzodazole

Note 17'': N-(1,1,2,2-tetrachloroethylthio)-cyclohexene-1,2-
dicarboxyimide

Note 18'': α -chloro- α -phenyl acetyl urea

Note 19'': 2-methyl carboxy-amino-benzimidazole

Note 20'': talc

Note 21'': titanium oxide

Note 22'': red iron oxide

Note 23'': colloidal silica

Note 24": xylene

Note 25": methyl isobutyl ketone

Note 26": n-butanol

The coating compositions obtained in Examples 19 to 58 and Comparative Examples 5 to 9 each was applied onto a test plate in about 200 μ dry thickness, and thus prepared test plate was attached to Discrotor, immersed in sea water (16° to 23°C) and rotated at a constant speed (peripheral speed about 30 knots) for 3 months (days and nights). Use-up rate of the coating was determined microscopically. The results are show in Table 2.

Table 2

Example	Initial film thickness μ	Clating useful rate μ/min thickness after 30 min μ	Used up film thickness μ
9	190	160	30
20	210	185	25
21	190	165	25
22	190	135	55
23	200	160	40
24	200	185	15
25	185	160	25
26	210	160	50
27	170	160	10
28	190	160	30
29	180	150	30
30	190	165	25
31	180	170	10
32	190	170	20
33	190	160	30
34	185	150	35
35	200	160	40
36	200	165	35
37	210	190	20
38	185	170	15
39	190	160	30
40	205	185	20
41	195	180	15
42	185	165	20
43	200	190	10
44	210	185	25
45	190	180	10
46	210	195	15
47	180	170	10
48	210	180	30
49	205	180	25
50	200	170	30
51	195	160	35
52	195	160	35
53	200	170	30
54	190	155	35
55	170	130	40
56	205	180	25
57	210	185	25
58	190	165	25
Comp. Ex.			
1	200	0	200
2	180	100	80
3	170	105	65
10	150	120	30
11	105	35	70

Table 2 shows the useful life and consumption of the coating film of the present invention. The film was prepared with an initial thickness of 190 to 210 μ and a coating rate of 1.0 to 1.5 μ/min , and the rate of use was 1.0 to 1.5 μ/min . The useful life of the film was determined by the amount of film used up to the point where the film was no longer usable. The useful life of the film was determined by the amount of film used up to the point where the film was no longer usable.

Table 3

Antifouling test

(surface area % adhered with submarine living)

Example	19	20	21	22	23	24	25	26	27	28	29	30	31
Duration (months)													
2	0	0	0	0	0	0	0	0	0	0	0	0	0
4	0	0	0	0	0	0	0	0	0	0	0	0	0
6	0	0	0	0	0	0	0	0	0	0	0	0	0
6	0	0	0	0	0	0	0	0	0	0	0	0	0
10	0	0	0	0	0	0	0	0	0	0	0	0	0
12	0	0	0	0	0	0	0	0	0	0	0	0	0
14	0	0	0	0	0	0	0	0	0	0	0	0	0
16	0	0	0	0	0	0	0	0	0	0	0	0	0
18	0	0	0	0	0	0	0	0	0	0	0	0	0
20	0	0	0	0	0	0	0	0	0	0	0	0	0
24	0	0	0	0	0	0	0	0	0	0	0	0	0
26	0	5	0	0	0	5	0	0	0	0	0	5	0
28	0	15	0	0	5	10	0	5	0	0	0	15	0
30	3	20	0	5	10	15	10	15	0	0	0	20	0

Table 3 (continued).

Antifouling test

(surface area % adhered with submarine living)

Example	32	33	34	35	36	37	38	39	40	41	42	43	44
Duration (months)													
2	0	0	0	0	0	0	0	0	0	0	0	0	0
4	0	0	0	0	0	0	0	0	0	0	0	0	0
6	0	0	0	0	0	0	0	0	0	0	0	0	0
6	0	0	0	0	0	0	0	0	0	0	0	0	0
10	0	0	0	0	0	0	0	0	0	0	0	0	0
12	0	0	0	0	0	0	0	0	0	0	0	0	0
14	0	0	0	0	0	0	0	0	0	0	0	0	0
16	0	0	0	0	0	0	0	0	0	0	0	0	0
18	0	0	0	0	0	0	0	0	0	0	0	0	0
20	0	0	0	0	0	0	0	0	0	0	0	0	0
24	0	0	0	0	0	0	0	0	0	0	0	0	0
26	5	0	0	0	0	0	0	0	0	0	0	0	0
28	15	0	5	0	0	0	0	3	0	0	0	0	0
30	20	0	15	10	0	3	0	10	10	5	0	0	3

Table 3 (continued)

Antifouling test

(surface area % adhered with submarine living)

Example	45	46	47	48	49	50	51	52	53	54	55	56	57	58
Duration (months)														
2	0	0	0	0	0	0	0	0	0	0	0	0	0	0
4	0	0	0	0	0	0	0	0	0	0	0	0	0	0
6	0	0	0	0	0	0	0	0	0	0	0	0	0	0
6	0	0	0	0	0	0	0	0	0	0	0	0	0	0
10	0	0	0	0	0	0	0	0	0	0	0	0	0	0
12	0	0	0	0	0	0	0	0	0	0	0	0	0	0
14	0	0	0	0	0	0	0	0	0	0	0	0	0	0
16	0	0	0	0	0	0	0	0	0	0	0	0	0	0
18	0	0	0	0	0	0	0	0	0	0	0	0	0	0
20	0	0	0	0	0	0	0	0	0	0	0	0	0	0
24	0	0	0	0	0	0	0	0	0	0	0	0	0	0
26	0	0	0	0	0	0	0	*	*	*	*	*	*	*
28	0	0	0	0	0	0	0	*	*	*	*	*	*	*
30	0	10	3	5	0	0	0	*	*	*	*	*	*	*

* ... unexamined

Table 3 (continued)

Antifouling test

Surface area % adhered with submarine living)

Comparative Example	7	8	9	10	11
Duration (months)					
2	0	0	0	0	0
4	0	30	0	0	0
6	100	80	0	0	0
6	100	100	0	0	0
10	100	100	0	0	0
12	stopped	100	10	5	0
14		stopped	30	20	0
16			100	70	30
18			100	100	100
20			100	100	100

Visual examination of surface conditions:

After conducting the aforesaid immersion test, the coated plate was examined by naked eyes on the surface conditions. No blisters and cracks were found on the coated plates of Examples 10 to 58. In Comparative Example 7, cracks were observed after 10 months' immersion test and in Comparative Example 8, blisters were observed after 10 months' immersion test.

The present invention thus provides a novel process for the preparation of metal-containing, hydroxyisocyanate resin composition which is very useful as resinous vehicle for an antifouling paint having excellent bonding function and well-balanced dissolution properties. This process is quite suitable for the preparation of such resin compositions with a variety of metal sources in comparatively higher yields. The present resin composition can be freely compounded with a variety of antifouling agents and thus obtained antifouling paints are characterized in resulting coatings which are free from blisters and iron corrosion and give excellent long-lasting antifouling effects.

Claims

1. A process for preparing metal-containing resin composition comprising reacting a mixture of A and a group containing base resin
2. A metal salt of a hydroxyisocyanate resin and a metal salt of a hydroxyisocyanate resin, in which the metal salt is a metal salt of a hydroxyisocyanate resin and a metal salt of a hydroxyisocyanate resin.
3. A process for preparing metal-containing resin composition comprising reacting a mixture of A and a group containing base resin

2. A process according to claim 1, wherein the metal is selected from the members belonging to Ib, IIa, IIb, IIIa, IIIb, IVa, IVb, Va, VIa, VIb, VIIa and VIII groups of Periodic Table.

3. A process according to claim 2, wherein the metal is selected from zinc, copper and tellurium.

4. A process according to claim 1, wherein the low boiling organic basic acid has a boiling point of 100 to 240 °C and the high boiling organic monobasic acid has a boiling point which is at least 20 °C higher than the boiling point of said low boiling organic basic acid.

5. A process according to claim 1, wherein the high boiling organic monobasic acid has an antifouling property.

6. A process according to claim 1, wherein the reaction is carried out in the presence of water, while removing the formed low boiling organic basic acid azeotropically with said water.

7. A process according to claim 1, wherein the low boiling organic basic acid is removed under reduced pressure.

8. A process according to claim 1, wherein the reaction is carried out in the presence of an organic solvent and the formed low boiling organic basic acid is removed out of the system azeotropically with said organic solvent.

9. An antifouling paint containing as resinous vehicle a metal containing resin composition prepared by the method wherein a mixture of

(A) acid group containing base resin.

(B) metallic salt of low boiling organic basic acid, in which the metal is selected from the members having 2 or more valence and lesser ionization tendency than those of alkali metals, and

(C) high boiling organic monobasic acid

is reacted at an elevated temperature while removing the formed low boiling organic basic acid out of the system.

10. An antifouling paint according to claim 9, wherein the metal is selected from the members belonging to Ib, IIa, IIb, IIIa, IIIb, IVa, IVb, Va, VIa, VIb, VIIa and VIII groups of Periodic Table.

11. An antifouling paint according to claim 10, wherein the metal is selected from zinc, copper and tellurium.

12. An antifouling paint according to claim 9, wherein the acid group containing base resin has an acid value of 25 to 350 mg KOH/g.

13. An antifouling paint according to claim 9, wherein the low boiling organic basic acid has a boiling point of 100 to 240 °C and the high boiling organic monobasic acid has a boiling point which is at least 20 °C higher than the boiling point of said low boiling organic basic acid.

14. An antifouling paint according to claim 9, wherein the high boiling organic monobasic acid has an antifouling property.

15. An antifouling paint according to claim 9, which further contains either one or combination of two or more of organic antifouling agent, inorganic antifouling agent, plasticizer, hydrolysis regulator, pigment, solvent and other conventional additives.



European Patent
Office

EUROPEAN SEARCH REPORT

Application Number

EP 88 20 0970

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. 4)
A	GB-A-2 058 801 (RHONE-POULENC) * Claims 1-18; page 3, lines 48-52 *	1	C 08 F 3/44 C 09 D 5/14
A	PATENT ABSTRACTS OF JAPAN, vol. 11, no. 365 (C-460)[2812], 27th November 1987; & JP-A-62 135 575 (KANSAI PAINT CO. LTD) 18-06-1987	1	

TECHNICAL FIELDS SEARCHED (Int. Cl. 4)

C 08 F
C 09 D

The present search report has been drawn up for all claims

EP FORM 1001 (12/1990)

Place of search	Date of completion of the search	Examiner
THE HAGUE	24-01-1989	FERMENTIER W.J.A.
<p>CATEGORY OF CITED DOCUMENTS</p> <p>X: particularly relevant if taken alone Y: particularly relevant if combined with another document of the same category A: technical background D: document cited for its disclosure P: prior art document</p> <p>1: this report is prior art in respect of invention 2: another patent document, but published only after the filing date 3: document cited in the application 4: document cited for its disclosure 5: document cited for its disclosure 6: document of the same patent family as the cited document</p>		

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